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Liquid Membrane Electrodes Responsive to Such Organic Anions as Antiseptics and Artificial Sweetenings

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A study was undertaken to evaluate the response and selectivity characteristics of liquid membrane electrodes responsive to organic anions such as antiseptics and artificial sweetenings using the Orion liquid ion-exchange electrode. 1-Decanol solutions of methyltrioctylammonium salts (Kao Quartamine T-08) of organic anions were used as liquid membrane components. The electrodes gave Nernstian responses for the solutions in a concentration range of 10^{-1} to at least 10^{-3} M and were useful at concentrations down to 10^{-4} M. The dissociation constant, pK_a , obtained from the pH response profile was in good agreement with that in the literature.

INTRODUCTION

Since the introduction of a liquid membrane electrode selective for calcium by Ross,¹⁾ many new electrodes of this type response to both cations and anions have undergone rapid expansion in recent years.^{2,3)} Of these, the liquid membrane electrodes based on the formation of ion pairs of high molecular weight quaternary ammonium cations with some anions were investigated.⁴⁻⁸⁾ Especially 1-decanol solutions of methyltricaprylammonium salts (Aliquot 336S) of inorganic and organic anions were effective as liquid membrane components in the preparation of electrodes that gave Nernstian responses for solutions in a concentration range of 10^{-1} to approximately 10^{-4} or 10^{-5} M.⁶⁻⁸⁾ These electrodes were found to be useful for the determination of such organic anions as amino acids and organic carbonic acids as well as inorganic ions.

Freiser *et al.* revealed that the equilibrium constants accounted for the interferences of iodine and organic acids with liquid membrane electrodes, after determining the distribution equilibria of tetrahexylammonium salts including these anions.⁹⁾ This shows an inherent limitation of selectivity of electrode response to ions of similar structure, while the organic responsive electrodes were very useful in the absence of interferences, and there has been relatively little published for the systems which respond primarily to organic ions. In this paper, we wish to report the evaluation of the electrodes responsive to antiseptics and artificial sweetenings.

EXPERIMENTAL

Reagents

Methyltrioctylammonium chloride (Kao Quartamine T-08) was kindly supplied

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from Kao Soap Co., Ltd. All other chemicals used were reagent grade materials. Stock solutions of organic anions (0.2 M) were prepared by neutralizing a known weight of the acid with sodium hydroxide solution to give a neutral solution. Imidazole solution was used for adjusting pH of the solution around neutral pH region.

Apparatus

The liquid membrane electrode utilized in this study was the nitrate ion-selective electrode (model 92-07) obtained from Orion Research, Inc. A millipore $10\ \mu$ Teflon membrane (LCWPO) was used to separate the organic and aqueous reference phases. The organic phase consisted of a 10 V/V per cent of solution of Kao Quartamine T-08 in 1-decanol which had been converted to the proper quaternary ammonium salt by repeated shaking with an aqueous 0.1 M solution of the potassium or sodium salt of the corresponding organic anion until chloride ion did not become detectable in an aqueous phase.

The internal aqueous reference phase consisted of a 0.1 M potassium chloride solution that was also 0.1 M in the potassium or sodium salt of the appropriate organic anion at pH region of 7.0-8.0. After preparation, the electrode was conditioned by immersion in 0.1 M solution of the salt to be measured for several hours and was stored in this manner when not in use.

All potentiometric measurements were made using a Beckman Research pH meter (model 1019) equipped with a Beckman saturated calomel electrode as the reference electrode. The potentiometric measurements were made under constant conditions by taking 25 ml of solution for each measurement at 25°C, immersing the electrodes to a constant depth in the solution.

RESULTS AND DISCUSSION

Response Characteristics

Each of the six electrodes was tested in the solutions buffered with imidazole around pH 7.0 over a concentration range of 10^{-1} to 10^{-5} M. The calibration curves of potential *vs.* concentration for the electrodes prepared are shown in Figs. 1 and 2. Equilibrium potentials were achieved considerably quickly (1-3 minutes) and values were reproducible to ± 0.5 mV at a high concentration of the anion.

As shown in Figs. 1 and 2, the potential response in each case gave a linear with logarithm of the organic anion concentration from 10^{-1} to at least 10^{-3} M. The change of the electrode response with concentration was large enough to be useful at concentrations down to 10^{-4} M. These results are summarized in Table I.

The electrode potential tended to drift slightly if measurements were made, following measurements of fairly interfering anions such as perchlorate and nitrate. As small change in the potential value on standing was observed, almost daily restandardization of all electrodes was required. These electrodes had the effective lifespan more than one month.

Effect of pH

Curve I in Fig. 3 shows the influence of pH on the potentials of the electrode responsive to dehydroacetate ion in its 10^{-2} M solution. The potentials did not change

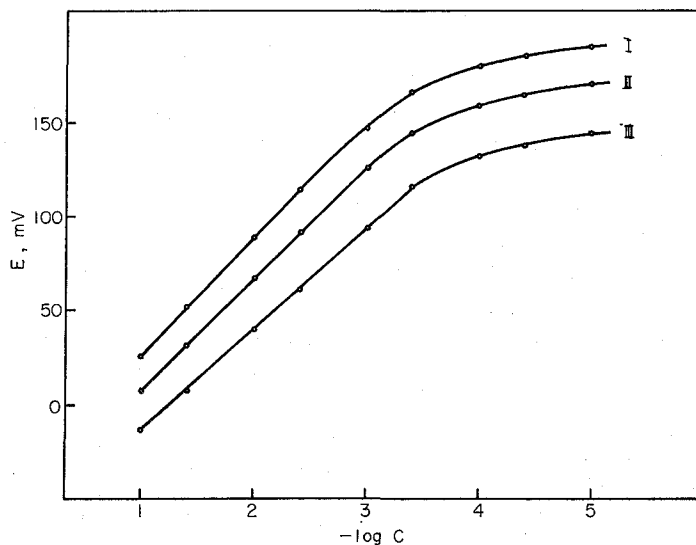


Fig. 1. Calibration curves for organic anion responsive electrodes
I; dehydroacetate, II; cyclohexylsulfamate, III; benzosulfimide

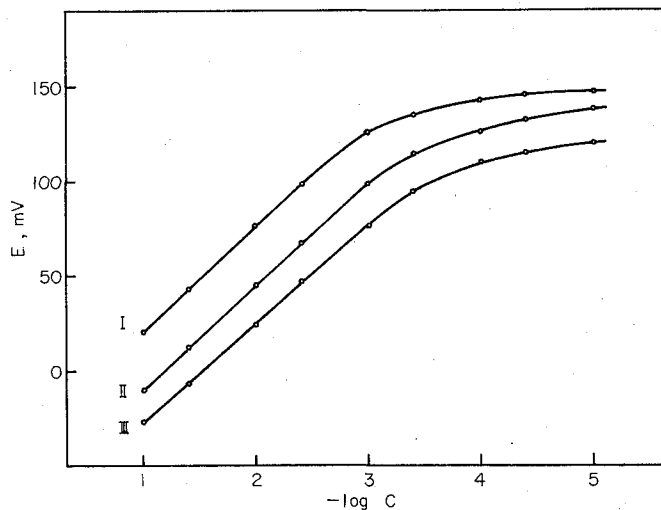


Fig. 2. Calibration curves for organic anion responsive electrodes
I; *p*-hydroxybenzoate, II; benzoate, III; salicylate

Table I. Behavior of Organic Anion-Responsive Electrodes

Electrode	Slope (mv/logC)	Concentration range of linear response	Useful concentration range	pKa
Dehydroacetate	58	10 ⁻¹ —10 ^{-3.0}	—10 ^{-4.0}	5.36
Benzoate	58	10 ⁻¹ —10 ^{-3.0}	—10 ^{-4.0}	4.19
<i>p</i> -Hydroxybenzoate	58	10 ⁻¹ —10 ^{-3.0}	—10 ^{-4.0}	4.58
Salicylate	55	10 ⁻¹ —10 ^{-3.4}	—10 ^{-4.0}	2.98
Cyclohexylsulfamate	58	10 ⁻¹ —10 ^{-3.4}	—10 ^{-4.0}	—
<i>o</i> -Benzosulfimide	54	10 ⁻¹ —10 ^{-3.4}	—10 ^{-4.0}	(2.32)

over pH range 6.8–10.0, but they increased sharply when the pH was measured below 6.0. This may be caused by the formation of non-ionic dehydroacetic acid. From this pH response profile, the dissociation constant, pK_a , of dehydroacetic acid was obtained.

The effect of pH on the potentials of the electrodes which respond to benzoic acid, salicylic acid, *p*-hydroxybenzoic acid and benzosulfimide was shown in Figs. 3 and 4, and the dissociation constants of these ions were similarly obtained. The dissociation constants obtained here were shown in Table I and these values were in good agreement with those in the literature. Inversely this indicates that the change in response with pH is attributable to the ability of the electrode to discriminate between the anionic and neutral forms of the species in question. Only the dissociation constant of benzo-

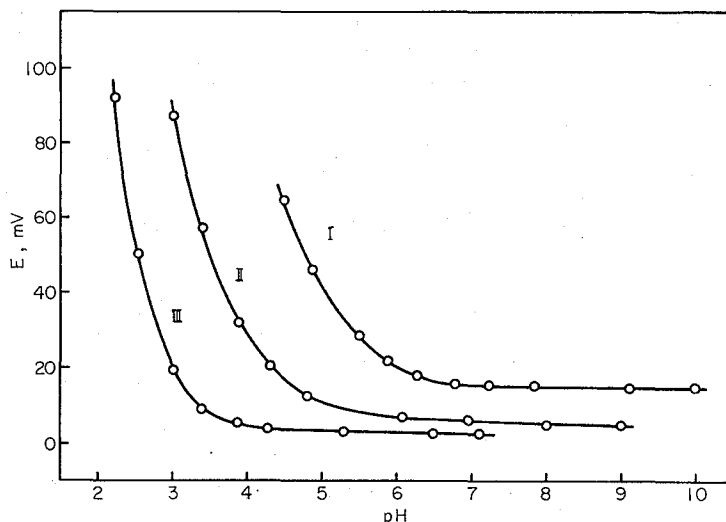


Fig. 3. The effect of pH on the potentials of organic anion responsive electrodes I; dehydroacetate, II; benzoate, III; salicylate

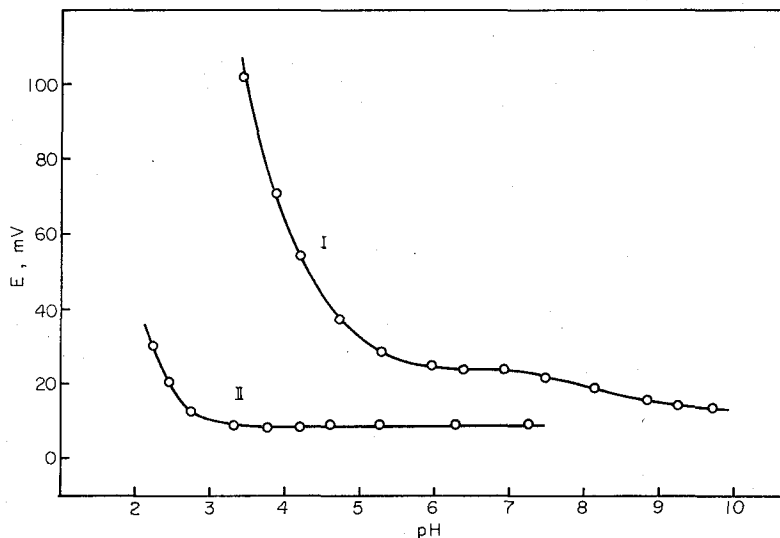


Fig. 4. The effect of pH on the potentials of organic anion responsive electrodes I; *p*-hydroxybenzoate, II; benzosulfimide

sulfimide is doubtful, because the interference of hydrogen ion may exist in such a lower pH range.

Selectivity Ratios

Interferences by other anions were determined by adding a sufficient amount of the interfering anion to a 10^{-2} M or 2×10^{-3} M standard test solution to give a potential difference of 5 to 50 mV from the pure test solution. Selectivity ratio, K , was calculated from the modified Eisenman equation,¹⁰⁾

$$E = E^\circ - (\text{slope}) \log(C_A + KC_i^{n/z}) \quad \text{or}$$

$$\Delta E = (\text{slope}) \log[1 + KC_i^{n/z}/C_A]$$

where C_A is the concentration of the anion A^{n-} , and C_i , that of the interfering anion of charge z^- . Table II summarizes these results in term of the logarithmic value of K , the selectivity ratio. The values for selectivity reported here are only relative and slightly depend on the factors such as the age of the electrode. In general, the extent of interference of any anion is qualitatively related to the extractability or formation constant of its ion association complex with the quaternary ammonium ion. These electrodes can not be considered as highly selective, but have a considerably wide range of useful measurements.

Table II. Selectivity Ratios for Various Interfering Anions Expressed as log K

Anion	Dehydro- acetate	Benzoate	<i>p</i> -Hydroxy- benzoate	Salicylate	Cyclohexyl- sulfamate	Benzo- sulfimide
Cl ⁻	-0.5	-1.1	-0.2	-2.4	-0.4	-1.1
NO ₃ ⁻	0.0	-0.4	0.3	-1.3	0.0	0.4
SO ₄ ²⁻	-0.8	-2.4	-2.0	-3.0	-0.8	-2.4
ClO ₄ ⁻	0.4	0.1	0.5	0.9		0.2
HCO ₃ ⁻	-1.4	-1.6	-0.6	-2.7	-1.0	-2.7
Acetate	-0.9	-1.3	-0.6	-2.5	-0.9	-1.7
<i>o</i> -Benzosulfimide	0.1	-0.1	0.3	-0.4	0.2	—
Dehydroacetate	—	-0.1	0.1	-1.0	0.1	-0.3
Cyclohexylsulfamate	0.0	-0.1	0.2	-0.8	—	-0.3
Sorbate	0.0	-0.1	0.1	-0.9	0.1	-0.2
Benzoate	0.0	—	0.2	-0.7	0.1	-0.1
<i>p</i> -Hydroxybenzoate	-0.3	-0.6	—	-1.9		-0.7

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